

UNIT - 4 FUELS

Syllabus: Introduction, calorific value, higher calorific value, lower calorific values, problems using Dulong's formula, proximate and ultimate analysis of coal sample and their significance, numerical problems, petroleum (refining-cracking), synthetic petrol (Fischer Tropsch and Bergius), petrol knocking, diesel knocking, octane and cetane ratings, anti-knocking agents, Introduction to alternative fuels (Bio-diesel, ethanol, methanol, natural gas, liquefied petroleum gas, compressed natural gas), Flue gas analysis by Orsat apparatus, rocket fuels.

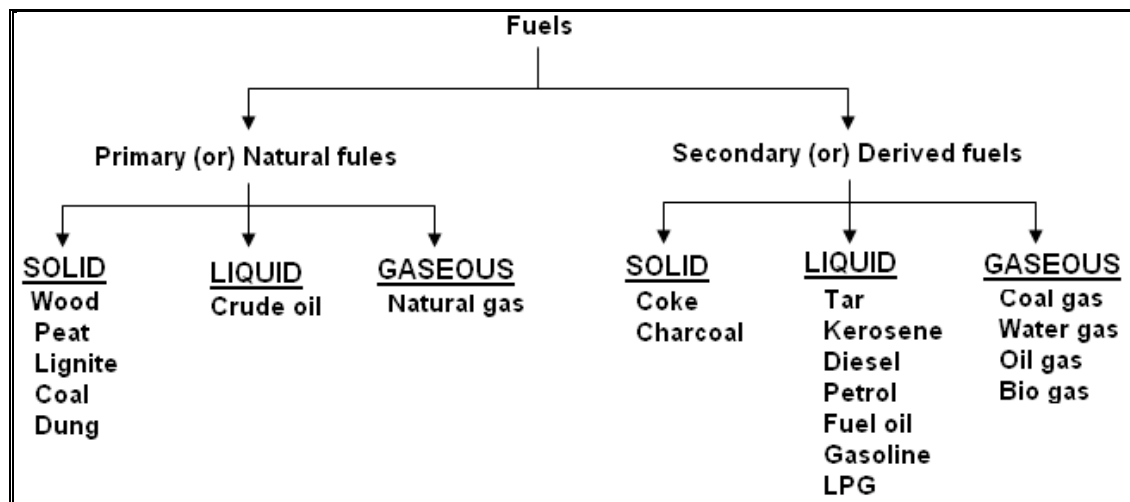
Φ Define a Fuel and Explain the classification of fuels with examples?

Fuel: Fuel is a combustible substance, containing carbon as main constituent, which on proper burning gives large amount of heat, which can be used economically for domestic and industrial purposes.



Classification of fuels:

- ★ On the basis of occurrence fuels are classified into primary and secondary.
- ★ Again each one is divided into three types based on their physical state.
- ★ Primary fuels are found in nature. Secondary fuels are produced from primary fuels



Φ What are the characteristics of good fuel (or) Ideal fuel?

While selecting an ideal fuel for domestic or industrial purpose we should keep in mind that the fuel selected must possess the following characteristic properties.

- 1) It should possess high calorific value.
- 2) It should have proper ignition temperature. The ignition temperature of the fuel should neither be too low nor too high.
- 3) It should not produce poisonous products during combustion. In other words, it should not cause pollution o combustion.
- 4) It should have moderate rate of combustion.
- 5) Combustion should be easily controllable i.e., combustion of fuel should be easy to start or stop as and when required.
- 6) It should not leave behind much ash on combustion.
- 7) It should be easily available in plenty.
- 8) It should have low moisture content.
- 9) It should be cheap.

10) It should be easy to handle and transport.

Φ **Discuss comparison between solid, liquid and gaseous fuels?**

Solid fuel	Liquid fuel	Gaseous fuel
1. Slow combustion and not easy to control it	Quick combustion and can be controlled	Combustion is rapid and burning can be controlled
2. Transportation is difficult	Transportation is easy through pipelines	Transportation is easy through pipe lines and containers
3. Storage is safe	There is risk in storing	There is greatest risk in storing
4. Calorific value is comparatively low	Calorific value is comparatively higher	Calorific value is highest
5. Cannot be used in internal combustion engines	Can be used in internal combustion engines	Can be used in internal combustion engines to lesser extent
6. On burning ash and more smoke are produced.	No ash is produced but Some flue gases are produced	No ash and no smoke are produced
7. More air pollution	Less air pollution	Least air pollution

Calorific Value:

Φ **What is calorific value? Give their units?**

Calorific value: It is defined as the total amount of heat liberated, when unit mass or unit volume of the fuel is completely burnt in air or oxygen.

Units of heat:-

- a) Calorie:- The amount of heat required to increase the temperature of 1 gm of water through one degree centigrade.
- b) Kilocalorie:- It is equal to 1000 calories. The quantity of heat required to rise the temperature of 1 Kg of water through one degree centigrade.
 $1 \text{ K.cal} = 1000 \text{ cals}$
- c) British thermal unit (B.Th.U.): - The quantity of heat required to rise the temperature of 1 pound of water through one degree Fahrenheit.
 $1 \text{ B.Th.U} = 252 \text{ cals} = 0.252 \text{ K.cal}$
- d) Centigrade heat unit (C.H.U.): - The quantity of heat required to rise the temperature of one pound of water through one degree centigrade.
 $1 \text{ K. cal} = 3.968 \text{ B.Th.U} = 2.2 \text{ C.H.U}$
For solids or liquid fuel: Calorie/gm (cal/gm) (or) Kilocalorie/Kg (K.cal/Kg) (or) B.Th.U/lb
For gaseous fuels: Kilocalorie/cubic meter (K.cal/m³) (or) B.Th.U/ft³

Φ **Define HCV & LCV. Give relationship between HCV & LCV.**

HCV: [Higher Calorific Value]: It is defined as the total amount of heat liberated, when unit mass or unit volume of the fuel is completely burnt and the products of combustion are allowed to cool to room temperature. Hydrogen is present in almost all the fuels. During determination of calorific value, hydrogen is converted into steam. Higher calorific value includes the latent heat of condensation of steam. HCV is also called Gross Calorific Value. [GCV].

LCV: [Lower Calorific Value]: It is defined as the total amount of heat liberated, when unit mass or unit volume of the fuel is completely burnt and the products of combustion are allowed to escape out into atmosphere. LCV is also called Net Calorific Value [NCV].

Relationship between HCV & LCV:

$$\text{LCV} = \text{HCV} - \text{latent heat of water vapour formed}$$

Since 1 part by mass of hydrogen produces 9 parts by mass of water.

$$\text{Hence LCV} = \text{HCV} - (\text{mass of hydrogen} \times 9 \times \text{latent heat of steam})$$

$$\text{LCV} = \text{HCV} - \left(\frac{H}{100} \times 9 \times \text{latent heat of steam} \right)$$

$$\text{LCV} = \text{HCV} - (0.09 H \times \text{latent heat of steam})$$

$$\text{LCV} = \text{HCV} - (0.09 H \times 587)$$

Where, H is % of Hydrogen

Latent heat of steam = 587 K.cal/Kg

Φ What is Dulong's formula? Derive an expression for theoretical calculation of Calorific value of fuel?

According to Dulong, the calorific value of fuel is the sum of the calorific values of all the elements present.

The calorific values of different elements are:

The calorific value of Carbon = 8080 cal/g

The calorific value of Hydrogen = 34500 cal/g

The calorific value of Sulphur = 2240 cal/g

The oxygen, if present in fuel, is assumed to be present in combined form with hydrogen, i.e., in the form of fixed hydrogen [H₂O].

The amount of hydrogen available for combustion = Total hydrogen – fixed hydrogen

Dulong's formula for calorific value from the chemical composition of a fuel is:

$$\text{HCV} = \frac{1}{100} \left\{ 8080 (C) + 34500 \left(H - \frac{O}{8} \right) + 2240 (S) \right\}$$

Analysis of coal:

In order to assess the quality of coal, it is subjected to two types of analysis.

1. Proximate analysis
2. Ultimate analysis

Φ Discuss in detailed about Proximate Analysis of coal? Write its significance.

Proximate analysis:-

It gives information about the practical utility of coal. It includes the determination of moisture, volatile matter, ash and fixed carbon.

a) Moisture content:- About 1 gram of finely powdered air dried coal sample is weighed in a crucible, and is heated in hot air oven up to 105-110°C. The crucible is left for 1 hr in the oven and then taken out, cooled in a desiccator and weighed. Loss in weight is reported as moisture.

$$\% \text{ of moisture} = \frac{\text{Loss in weight}}{\text{Wt. of coal taken}} \times 100$$

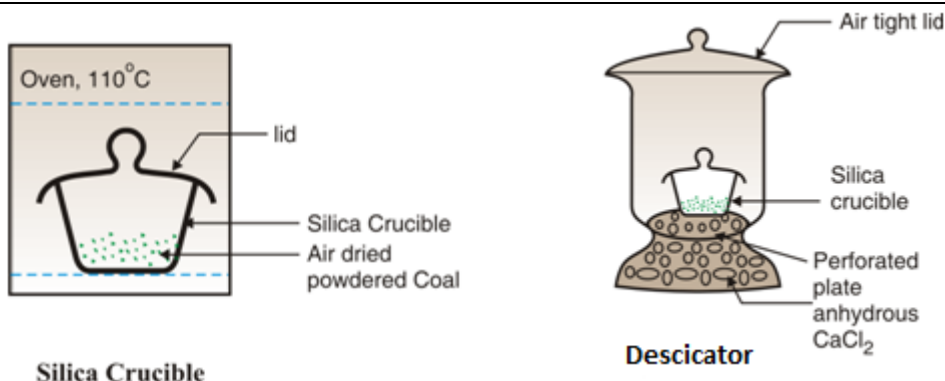
Importance of moisture:-

1. It increases the cost and transportation charges.

2. It quenches the fire in the furnace. Presence of 10% moisture produces less fly ash.
3. Moisture lowers the calorific value.

b) Volatile matter:- Dried coal is taken in a crucible and covered with a lid. It is heated in a furnace up to $925 \pm 20^\circ\text{C}$ for 7 min. The crucible is then taken out and cooled first in air, then inside desiccators and weighed again. Loss in weight is reported as percentage of volatile matter.

$$\% \text{ of volatile matter} = \frac{\text{Loss in weight}}{\text{Wt. of coal taken}} \times 100$$



Importance of volatile matter:-

1. Volatile matter contains combustible gases like CO , H_2 , CH_4 and hydrocarbons and non combustible gases don't add to the heat value.
2. Higher volatile content is undesirable because most of it escapes out as vapour.
3. Coal with high volatile matter burns with long flame, high smoke and low calorific value.
4. A furnace with small combustion volume is not suitable for burning coal with high volatile matter. Because it burns with high rates of burning.
5. For coke making, coals containing high volatile matter and very low volatile matter are not suitable.

c) Ash:- Known amount of coal is burnt in an open crucible at $700\text{--}750^\circ\text{C}$ for half an hour in a furnace. Heating, cooling and weighing are repeated till a constant weight is obtained.

$$\% \text{ of ash} = \frac{\text{Wt. ash formed}}{\text{Wt. of coal taken}} \times 100$$

Importance of determination of ash content:-

1. It reduces the calorific value of coal.
2. It hinders the flow of air and heat so that efficiency of coal decreases.
3. It also increases transporting, handling and storage costs. Ash disposal is another additional cost.
4. Lumps of ash obstruct the grate so that air supply for burning coal is reduced.

d) Fixed carbon:- After determining all the above, the remaining material is known as fixed carbon. It is obtained by subtraction of volatile matter, moisture and ash from 100.

$$\% \text{ fixed carbon} = 100 - \% \text{ of (moisture + volatile matter + ash)}$$

% fixed carbon helps in designing the furnace and shape of the fire – box.

Higher the % fixed carbon, greater is the calorific value.

Hence, A good quality coal has High calorific value. For High calorific value, coal

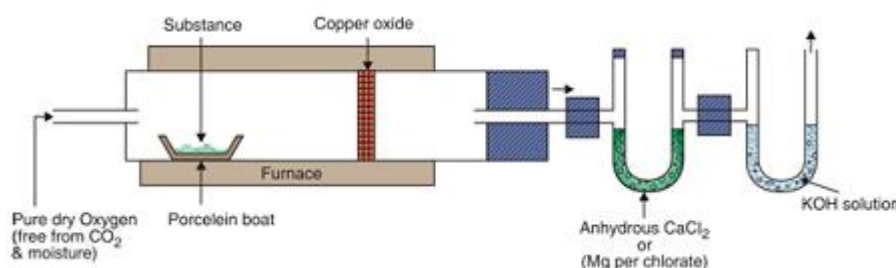
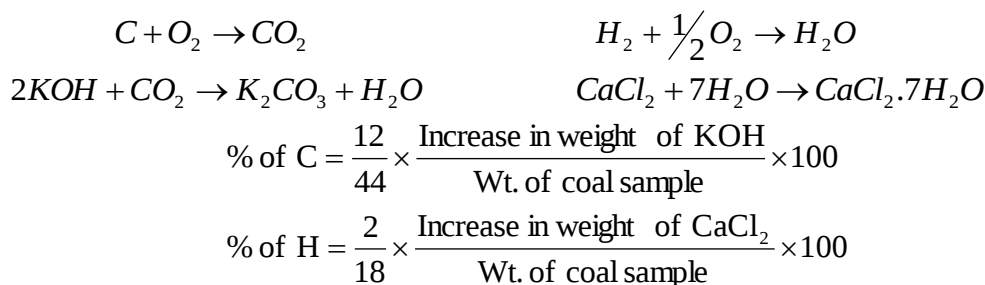
- must contain
1. Low Moisture content
 2. Low Volatile matter.

3. Low Ash content.
4. More Fixed Carbon.

Φ Discuss in detailed about Ultimate Analysis of coal ? Write its significance.

1. Determination of C and H:-

- About 1-2 gm of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus.
- C and H of the coal are converted into CO_2 and H_2O respectively.
- The gaseous products of combustion are absorbed respectively in KOH and CaCl_2 tubes of known weights.
- The increases in weights of these are determined.



Importance:-

- Greater the percentage of C and H better is the quality and calorific value of coal.
- The % C forms the basis of classification of coal.
- % 'H' is mostly associated with the volatile matter and hence it affects the use to which the coal is put.

2. Determination of Nitrogen:-

- ✍ About 1 gm of accurately weighed powdered coal is heated with concentrated H_2SO_4 along with K_2SO_4 in a long necked flask (Kjeldahl flask).
- ✍ After the solution becomes clear, it is treated with excess of KOH and the liberated ammonia is distilled over and absorbed in a known volume of standard acid solution.
- ✍ The unused acid is then determined by back titration with standard NaOH solution.
- ✍ From the volume of acid used by ammonia liberated, the % N in coal is calculated as

$$\% \text{ of N} = \frac{1.4 \times N \times \text{Vol. of acid}}{\text{Wt. of coal}}$$

Where, N = Normality of acid.



LIQUID FUELS:

Φ What are advantages and disadvantages of liquid fuels?

Advantages:

- 1) They possess higher calorific value per unit mass than solid fuels.
- 2) They burn without dust, ash, clinkers, etc.
- 3) Their firing is easier and also fire can be extinguished easily by stopping liquid fuel supply.
- 4) They are easy to transport through pipes.
- 5) They can be stored indefinitely without any loss.
- 6) They are clean in use and economic to handle.
- 7) Loss of heat in chimney is very low due to greater cleanliness.
- 8) They require less excess air for complete combustion.
- 9) They require less furnace space for combustion.

Disadvantages:

- 1) The cost of liquid fuel is relatively much higher as compared to solid fuel.
- 2) Costly special storage tanks are required for storing liquid fuels.
- 3) There is a greater risk of fire hazards, particularly, in case of highly inflammable and volatile liquid fuels.
- 4) They give bad odour.
- 5) For efficient burning of liquid fuels, specially constructed burners and spraying apparatus are required.

Petroleum or crude oil:

- Petroleum or crude oil is dark greenish-brown, viscous oil found deep in earth's crust.
- It is composed of various hydrocarbons together with small amounts of organic compounds containing oxygen, nitrogen and sulphur.
- The oil is, usually, found floating upon a layer of brine and has a layer of gas on top of it.
- The calorific value of petroleum is about 40,000 kJ/kg.

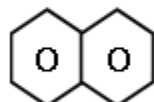
Composition:

The average composition of crude petroleum is C = 80 – 87%; H = 11.5 – 15%; S = 0.1 – 3.5%; N = 0.4 – 0.9 %; O = 0.1 – 0.9%.

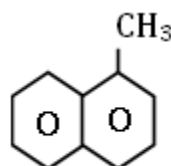
Classification of petroleum:-

The following types are three principle varieties of petroleum.

- 1) **Paraffinic-base type crude** is mainly composed of the saturated hydrocarbons from CH_4 to $\text{C}_{35}\text{H}_{72}$ and a little of the naphthalenes and aromatics. The hydrocarbons from $\text{C}_{18}\text{H}_{38}$ to $\text{C}_{35}\text{H}_{72}$ are semi-solids, called 'waxes'.
- 2) **Asphaltic-base type crude** contains mainly cyclo paraffins or naphthalenes with smaller amount of paraffins and aromatic hydrocarbons.



Napthalene



Methyl Napthalene

- 3) **Mixed-base type crude** contains both paraffinic and asphaltic hydrocarbons and are, generally, rich in semi-solid waxes.

Φ Explain about Refining of crude oil (or) Petroleum:

- ✍ The crude oil is separated into various fractions by fractional distillation and finally converted into desired specific products.
- ✍ The process is called “refining of crude oil” and the plants set up for the purpose, are called the oil refineries.
- ✍ The process of refining involves the following three steps:

Step-1:- Separation of water (Cottrell’s process):

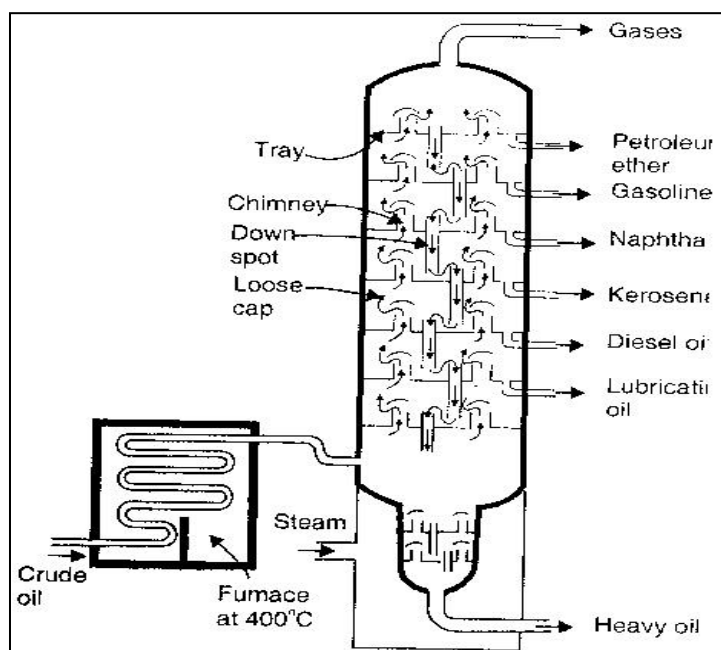
- The crude oil is in the form of stable emulsion of oil and salt water.
- Water is separated from oil by Cottrell’s process.
- First the emulsified water along with salts dissolved, is removed by passing the crude oil between highly charged electrodes.
- The colloidal water droplets unite on positive electrode to form large drops which separate from oil.

Step-2:- Removal of harmful sulphur compounds:

- In this step, the oil is treated with copper oxide.
- Sulphur and its compounds are converted into solid copper sulphides.

Step-3:- Fractional distillation:

- ◆ The crude oil is then heated to about 400°C in an iron retort, whereby all volatile constituents, except the residue are evaporated.
- ◆ The hot vapours are then passed up a “fractionating column”, which is a tall cylindrical tower containing a number of horizontal stainless steel trays at short distances.
- ◆ Each tray is provided with small chimney, covered with a loose cap.
- ◆ As the vapours go up, they become gradually cooled and different products are obtained at different heights of the column.



Various fractions with boiling range, approximate composition and uses :

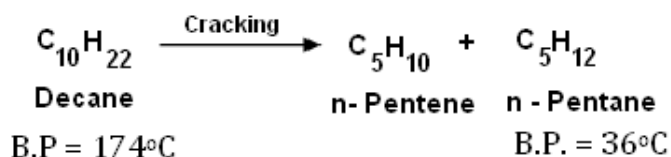
Name of fraction	Boiling range ($^{\circ}\text{C}$)	Approximate Composition in terms of hydrocarbons containing C-atoms	Use
Uncondensed gases	Below 30	$\text{C}_1 - \text{C}_4$	As domestic and industrial fuel under the name LPG
Petroleum ether	30 – 70	$\text{C}_5 - \text{C}_7$	As a Solvent
Gasoline or petrol	40 – 120	$\text{C}_5 - \text{C}_9$	Fuel for IC engines, Dry Cleaning solvent

Naphtha	120 – 180	C ₉ – C ₁₀	As solvent for paints and varnishes
Kerosene oil	180 – 250	C ₁₀ – C ₁₆	Fuel for stoves, jet engine fuel and for preparing lab gas
Diesel oil	250 – 320	C ₁₅ – C ₁₈	Diesel engine fuel
Heavy oil	320 – 400	C ₁₇ – C ₃₀	Fuel for ships and for conversion to gasoline by cracking.

Φ Write a note on Cracking:

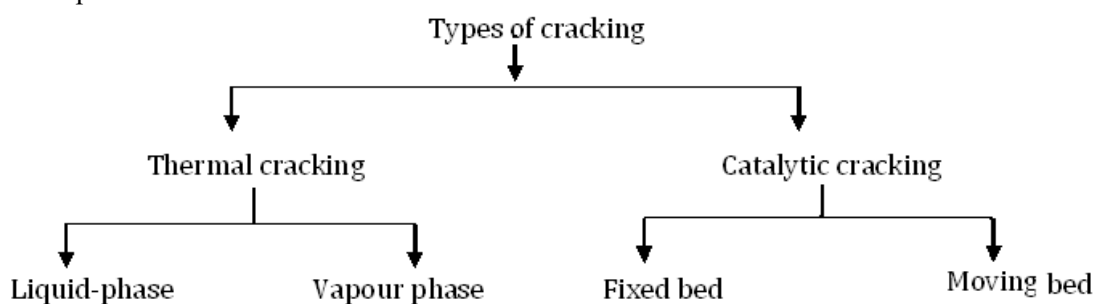
Cracking

Cracking is defined as the decomposition of high molecular weight hydrocarbons of high boiling points into simpler, lower molecular weight hydrocarbons of low boiling points.



Importance:

- ✓ Of all the fractions obtained by fractionation of petroleum, gasoline has the highest demand as a motor fuel. It is called straight run gasoline.
- ✓ Also the quality of so-called 'straight-run' gasoline is not so good.
- ✓ Hence, it is used only after suitable blending.
- ✓ For instance, the petrol made by cracking has far better characteristics (as far as the IC engine is concerned) than 'straight-run' petrol.



Thermal cracking:

- ✓ When the heavy oils are subjected to high temperature and pressure in the absence of catalyst, it is called thermal cracking.
- ✓ In thermal cracking, the bigger hydrocarbon molecules break down to give smaller molecules of the paraffin, olefins plus some hydrogen.
- ✓ It is of two types' viz. liquid and vapour phase thermal cracking.

A comparative account of these two is given in the following table.

Comparison of Liquid and Vapour phase Thermal Cracking

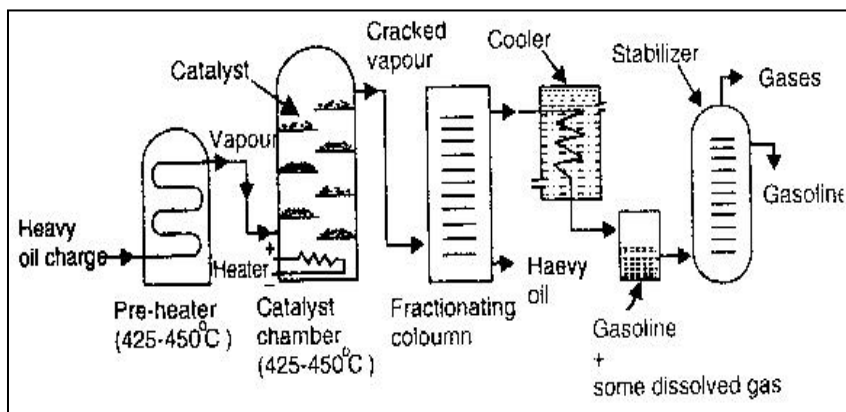
Characteristic	Liquid phase thermal cracking	Vapour phase thermal cracking
Cracking temperature	475–530°C	600–650°C
Pressure	100 kg/cm ²	10–20 kg/cm ²
Yield of petrol	50–60%	70%
Octane rating of petrol	65–70	(>70) ∴ Better antiknock characteristics
Criteria	None Any heavy oil can be used	Oil should be readily vaporized
Time required for cracking	More	Less

Catalytic cracking:

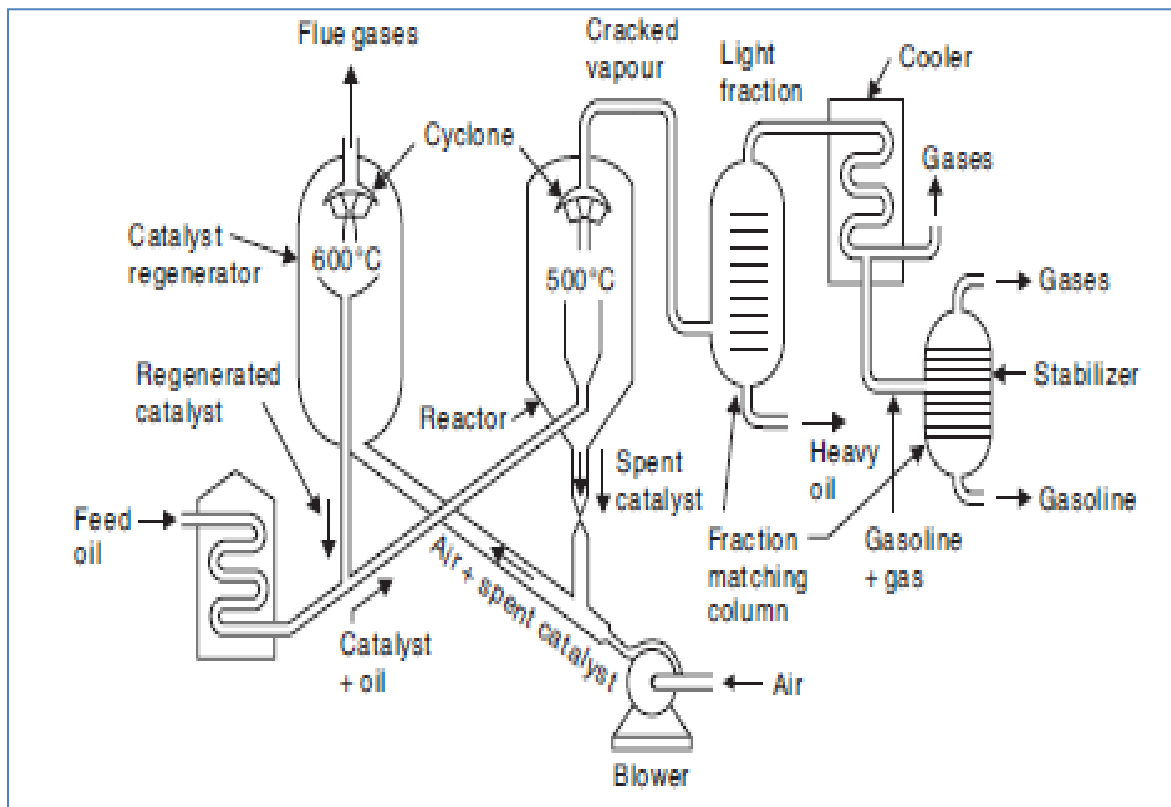
- ▲ The quality and quantity of gasoline produced by cracking can be greatly improved by using a suitable catalyst like aluminium silicate, $\text{Al}_2(\text{SiO}_3)_3$ or alumina, Al_2O_3 .
- ▲ Catalytic cracking requires much lower temperatures and pressures compared to thermal cracking.
- ▲ There are two types of catalytic cracking, viz. Fixed bed and Moving bed catalytic cracking.

Φ Explain with a neat diagram Fixed bed catalytic cracking?

- ✓ The heavy oil charge is passed through a preheater where it is heated up to 425 – 450°C.
- ✓ The hot vapours are then passed over a fixed bed of catalyst chamber maintained at about 425 – 450°C and 1.5 kg/cm² pressure.
- ✓ During their passage through the tower, about 40% of the charge is converted into gasoline and about 2-4% C is formed.
- ✓ The latter gets adsorbed on the catalyst bed.
- ✓ The catalyst, after 8 to 10 hours, stops functioning, due to the deposition of black layer of carbon formed during cracking.
- ✓ This is re-activated by burning off the deposited carbon.
- ✓ During the re-activation interval, the vapours are diverted through another catalyst chamber.



Φ Explain with a neat diagram Moving bed catalytic cracking?



- In moving bed catalytic cracking, the feed oil is first passed through a preheater.
- The pre-heated oil vapours along with very finely powdered catalyst are then passed in a reactor which is maintained at a temperature of 500°C for catalytic cracking.
- The cracked oil vapours are then passed to the fractionating column where heavy oil is separated.
- The vapours are then passed through the cooler where gasoline condenses along with some gases.
- This is then sent to a stabilizer where the dissolved gases are removed and pure gasoline is recovered.
- The main components along with their functions are discussed with the help of the figure.
 1. Cyclone allows only the cracked oil vapours to pass on to the 'fractionating column', but retains all the catalyst powder in the reactor itself.
 2. The catalyst powder gradually becomes heavier, due to coating with carbon, and settles to the bottom, from where it is forced by an air blast to regenerator (maintained at 600°C).
 3. In regenerator, carbon is burnt and the regenerated catalyst then flows through stand-pipe for mixing with fresh batch of incoming cracking oil.

Φ What are the Advantages of catalytic cracking over thermal cracking?

Catalytic cracking has a number of advantages:

1. The production cost is very less since high temperatures and high pressures are not needed.
2. The yield of petrol is higher.
3. The quality of petrol produced is better.
4. No external fuel is necessary for cracking. The heat for cracking is derived by burning the carbon deposited on the catalyst.
5. The product contains less sulphur compounds.
6. The percentage of gum and gum forming compounds is very low.

The octane number of cracked gasoline is higher compared to straight-run gasoline. It is due to presence of branched paraffins and aromatic hydrocarbons in cracked gasoline.

Synthetic petrol:

In view of the greater demand for petrol the synthetic methods gain importance. The following three methods are important synthetic processes for making petrol.

Polymerization: this method is opposite to cracking. The gases obtained as a by-product from cracking of heavy oils, etc., contain olefins (like ethylene, propene and butanes) and alkanes (such as methane, ethane, propane and butane). When this gaseous mixture is subjected to high pressure and hightemperature, with or without the presence of catalyst, they polymerizes to form higher hydrocarbons, resembling gasoline, called as polymer gasoline.

The polymerization is of two types:

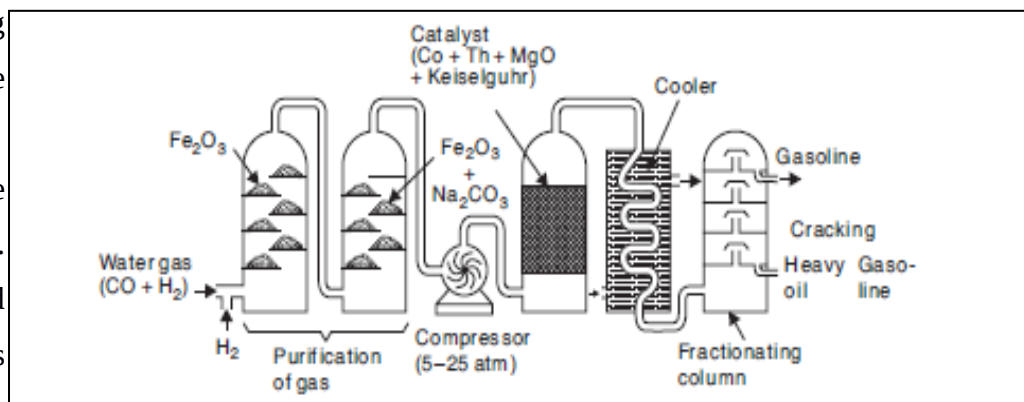
i) Thermal polymerization: In this process the polymerization of cracked gases is carried out at 500-600 ° C and 70-350 kg/cm² pressure. The product is gasoline and gas oil mixture which are separated by fractionation.

ii) Catalytic polymerization: This is carried out in presence of catalyst like phosphoric acid. In this case, lower temperature of 150-200 ° C is employed. Products are gasoline and un – polymerized gases. The latter is separated and recycled for polymerization.

Φ Discuss Fischer-Tropsch method of manufacture of Synthetic Petrol?

Water gas (CO+H₂), produced by passing steam over preheated (at 1200 C) hard coke, is mixed with hydrogen.

The gas is purified by passing through FeO (to remove H₂S) and then into a mixture of Fe₂O₃ + Na₂CO₃ (to remove organic sulphur compounds). The purified gas is compressed to pressure of 30 atmospheres and then led through a converter

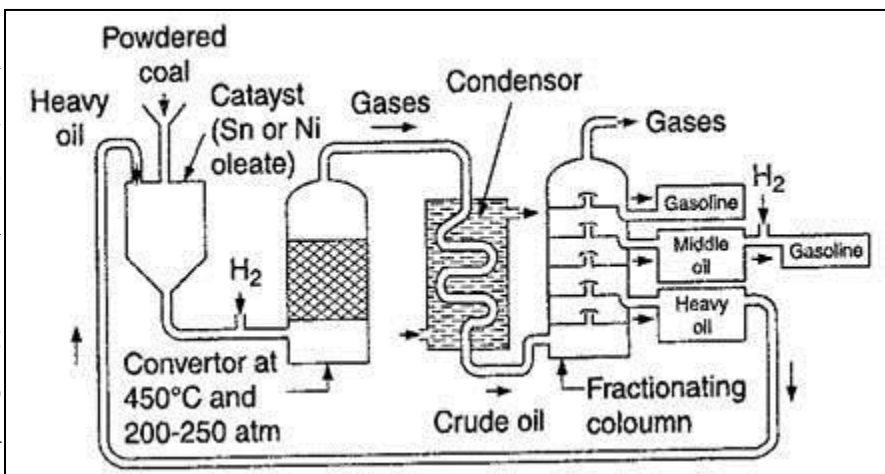


containing a catalyst, which is a mixture of 100 parts of cobalt, 5 parts of thorium, 8 parts of magnesia, and 200 parts of keiselguhar-earth, maintained at about 200-300 ° C. A mixture of saturated and unsaturated hydrocarbons results: The reaction is exothermic as such the hot gaseous mixture is led to a cooler, where a liquid resembling crude oil is obtained. The crude oil thus obtained is then fractionated to yield: (i) gasoline, and (ii) high-boiling heavy oil. The heavy oil is reused for cracking to get more gasoline.

Φ What do you mean by hydrogenation of coal? How Synthetic petrol is manufactured by Bergius Process? Or How solid fuel is converted into liquid fuel? Explain in detail.

Bergius Process:

The low ash coal is finely powdered and made into a paste with heavy oil and then a catalyst (composed of tin or nickel oleate). The paste is heated in a converter with hydrogen at 450 ° C and under a pressure 200-250 atm for about 1 1/2 hours, during which hydrogen combines with coal to form saturated hydrocarbons. They decompose at prevailing high temperature



and pressure to yield low boiling liquid hydrocarbons. The released gases from the reaction vessel are led to condenser, where a liquid resembling that of crude oil is obtained, which is then fractionated to get: i) gasoline, ii) middle oil, and iii) heavy oil. The latter are used again for making paste with fresh coal dust. The middle oil is hydrogenated in vapor-phase in presence of a solid catalyst to yields more gasoline. The yield of gasoline is about 60% of the coal dust used.

KNOCKING

- ✓ The characteristic rattling sound produced in internal combustion engine due to immature ignition is known as knocking.
- ✓ This situation occurs when compression ratio exceeds certain limit.
- ✓ Fuel mixture is heated to beyond ignition temperature which leads prior combustion than the sparking ignition.

Influence of chemical structure on fuel knocking:

- ★ As the length of the carbon chain increase, knocking tendency increases.
Ex: n- butane < n – pentane < n – hexane < n – heptane
- ★ Straight chain paraffins have more knocking property than branched chain alkanes.
Ex: 2, 2 – dimethyl pentane < 2- methyl hexane < n- heptane
- ★ Aromatic compounds like benzene and toluene have poor knocking property.
- ★ In general, the order of knocking property of various compounds is
Aromatic < Cyclo paraffins < Olefins < Branched alkanes < Straight chain alkanes.

Φ Explain about Petrol Knocking : [Gasoline knocking]:

The performance of motor car is measured in terms of Km/L of petrol, which depends on the quality of the fuel. Important method of obtaining more power from petrol is increasing the compression ratio of the engine.

$$\text{Compression ratio of engine} = \frac{\text{Initial volume of petrol and air mixture sucked into cylinder}}{\text{Final volume of petrol and air mixture after compression}}$$

Increase in the compression ratio of the engine, increases the efficiency of the engine. In the cylinder, combustion reaction is initiated by a spark as a result flame spreads rapidly and smoothly through gaseous

mixture. By this petrol undergoes combustion under thermal conditions and the pressure increases inside the cylinder. However, beyond a particular compression ratio, the -mixture of air and petro suddenly bursts into flames. This process is accompanied by a sharp knock in the internal combustion engine due to explosive combustion producing a shock wave which lose its energy by hitting the walls of the cylinder and piston. As a result a rattle sound is heard which is referred as knocking.

Knocking is defined as the production of shock wave in an IC engine due to explosive combustion of mixture of petrol and air which increases compression ratio beyond a certain value leading to rattle sound.

Effects of Knocking:

Knocking causes the following effects.

- 1) Produces undesirable rattling sound.
- 2) Decreases efficiency of engine and power out put.
- 3) Increases the fuel consumption.
- 4) Causes the mechanical damage to engine parts.
- 5) The driving becomes rather unpleasant.

Φ Explain about Diesel knocking?

The diesel engine work on the principle of compression. Air is drawn into the cylinder and compressed and the temperature rises to 500°C . The fuel is injected at this point as in finely divide spray hydrocarbons in the fuel absorb heat from the air vapourise and burn on attaining ignition temperature. Knocking in diesel engine occur due to ignition delay which is caused by the chemical nature of hydrocarbons in diesel i.e; straight chain hydrocarbons have shorter ignition delay than branched and aromatics hydrocarbons.

Ignition delay is caused because time is required for vapourization of fuel and raising the temperature of the vapour to its ignition temperature i.e; accumulation of fuel in the engine which leads to explosive combustion. This is called diesel knocking.

The substances added to control knocking is called as anti knocking agents. These substances improve the cetane number of diesel. Cetane number can be improved by adding substance called dopents like ethyl nitrate ,acetone , acetone peroxide which help in starting engine.

Φ What are Anti knocking agents? Give examples.

- ★ Some chemicals are added to fuel to improve its anti knocking properties. These additives are known as anti knocking agents.
- ★ The typical anti knocking agents in use are
 - a) Tetra ethyl lead (TEL)
 - b) Methyl cyclo penta dienyl manganese tricarbonyl (MMT)
 - c) Ferrocene
 - d) Iron penta carbonyl
 - e) Toluene
 - f) Iso octane

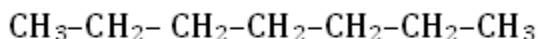
TEL:

- ✓ It is a colourless and poisonous liquid.
- ✓ About 0.5 ml of TEL per litre is added.
- ✓ TEL stops knocking by generating free radical inhibitors (Pb & PbO).
- ✓ But the Pb & PbO contaminate air as well as spoil engine parts.

- ✓ Now-a-days, it is out of use.
- ✓ In place of TEL, MMT is used in old cars designed for TEL.
- ★ Cetane number is improved by adding ethyl nitrite, ethyl nitrate, iso amyl nitrate and acetone peroxide.

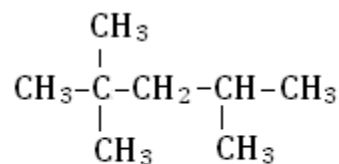
Φ Define Octane number? Explain in detailed.

- ✍ Anti knocking property of a fuel is expressed in terms of octane number.
- ✍ n – Heptane knocks very badly and an anti knocking property value zero is assigned to it where as iso octane has very high anti knocking property. So, its value is assigned as 100.



n - heptane

Anti knocking value = 0



Iso octane

Anti knocking value = 100

- ✍ Octane number is defined as the percentage of iso octane in a mixture of iso octane and n- heptane which has same knocking characteristics as that of test fuel under same set of conditions.

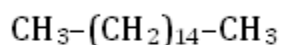
Ex: Octane number of test petrol is supposing 77. It means that the knocking properties of the test petrol are similar to that of a fuel which contains 77% iso octane and 23% n – heptane.

- ♠ Higher the octane number, greater is the anti knocking property of fuel (good fuel).

Example	Octane number
Benzene	106
Iso pentane	90
Cyclo hexane	77
n – pentane	62
n – hexane	26

Φ Define Cetane number? Explain in detailed.

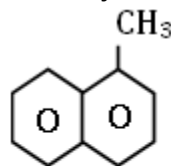
- ✍ Quality of diesel is expressed in terms of Cetane number.
- ✍ If the diesel undergoes ignition as soon as it is injected, it is good fuel.
- ✍ It should have very short interval between injection and ignition.
- ✍ The hydrocarbon Cetane (n – hexa decane) has a very short ignition delay and an arbitrary value of 100 has been assigned to it where as α – methyl naphthalene has very long ignition delay and hence 0 value is assigned to it.



n - hexa decane

Cetane

Anti knocking value = 100



α - Methyl Naphthalene

Anti knocking value = 0

- ✍ Cetane number of a diesel fuel may be defined as the percentage of Cetane in a mixture of Cetane and α – methyl naphthalene which has same ignition characteristics of test fuel under same set of conditions.
- ✍ Cetane number of various hydro carbons is in the following order.

Aromatics < Branched chain alkanes < Alkenes < Cyclo paraffins < n- alkanes

- ✍ The hydrocarbon with good Cetane number has poor octane number. A good fuel to diesel engine is a bad fuel to petrol engine.

Φ **Differentiate Octane number and Cetane number.**

Octane number		Cetane number	
1.	Octane referred for petrol	1.	This is referred for diesel
2.	Petrol with straight chain alkanes has lower octane number.	2.	Diesel with straight chain alkanes has higher cetane number.
3.	Low octane petrol in petrol engine produces loud cracking noise.	3.	Low cetane diesel in diesel/engine produces rattling metals noise and intense vibrations.
4.	Sudden combustion of hydrocarbons produces knocking in petrol engine.	4.	Delay in combustion causes knocking in diesel engine.
5.	Combustion decreasing chemicals are added in petrol to increase octane number.	5.	Combustion rate increasing chemicals added in diesel to increase cetane number.
6.	Octane number is considered to lower mol. wt. alkanes	6.	This is considered for mainly higher mol.wt. alkanes.

Gaseous fuels:

Gaseous fuels occur in nature, besides being manufactured from solid and liquid fuels.

Φ **What are the advantages and disadvantages of gaseous fuels ?**

Gaseous fuels due to ease and flexibility of their applications, possess the following advantages over solid or liquid fuels :

- 1) They can be conveyed easily through pipelines to the actual place of need, thereby eliminating manual labour in transportation.
- 2) They can be lighted at ease.
- 3) They have high heat contents and hence help us in having higher temperatures.
- 4) They can be pre-heated by the heat of hot waste gases, thereby affecting economy in heat.
- 5) Their combustion can readily be controlled for change in demand like oxidizing or reducing atmosphere, length flame, temperature, etc.
- 6) They are clean in use.
- 7) They do not require any special burner.
- 8) They burn without any shoot, or smoke and ashes.
- 9) They are free from impurities found in solid and liquid fuels.

Disadvantages:

- 1) Very large storage tanks are needed.
- 2) They are highly inflammable, so chances of fire hazards in their use is high.

Φ **Write a short note on Natural gas.**

- ✓ Natural gas is obtained from wells dug in the oil bearing regions .

- ✓ When natural gas occurs along with petroleum in oil wells it is called 'wet gas'.
- ✓ The wet gas is treated to remove propane, propene, butane and butene which are used as LPG.
- ✓ On the other hand when the gas is associated with crude oil, it is called as 'dry gas'.
- ✓ The natural gas is purified to remove objectionable ingredients such as water, dust, H_2S , CO_2 , N_2 and heavier liquefiable hydrocarbons.
- ✓ The approximate composition of natural gas is $CH_4 = 70-90\%$; $C_2H_6 = 5-10\%$; $H_2 = 3\%$; and the remainder = $CO + CO_2$
- ✓ Calorific value = $12000-14000 \text{ Kcal/m}^3$

Uses:

- ✓ It is an excellent domestic fuel and can be conveyed over very large distances in pipe lines.
- ✓ A large number of chemicals are synthesized from natural gas
- ✓ It is also used as raw material for the manufacture of carbon black and hydrogen
- ✓ Synthetic proteins are obtained by micro biological fermentation of methane

Φ Write a short note on CNG (Compressed natural gas).

- ❖ CNG is natural gas compressed to a high pressure of about 1000 atmospheres.
- ❖ It is an odourless, non-toxic gaseous mixture.
- ❖ CNG is measured in units of Gasoline Gallon Equivalent (GGE).
- ❖ The composition of CNG is CH_4 (90%), Other constituents are ethane, propane, gases like N_2 , CO etc..

Properties:

- ❖ Light weight, gaseous fuel. It mixes with air easily.
- ❖ It has a high auto-ignition temperature ($540^\circ C$) and narrow range of flammability.
- ❖ CNG does not contaminate with lubricating oils, thus increases the life of the IC engine.
- ❖ It requires more space for storage.
- ❖ The calorific value of CNG is 900 KJ/mole

Uses:

1. Majorly used as fuel in automobiles like cars, autos, trucks, buses etc..
2. It is also used as fuel for locomotive diesel generators to generate electricity, that drive the motors of trains.

Φ Write a short note on LPG (Liquified petroleum gas).

- It is also called as Bottled Gas (or) Refinery Gas.
- LPG is obtained as a by-product during the cracking of heavy oils or from natural gas.
- The main constituents of LPG are n-butane, iso-butane, butylene and propane
- LPG is supplied under pressure in containers under the trade name like Indane, Bharat gas, H.P etc..
- LPG is dehydrated and desulphurised.
- Its Calorific value is about 27800 Kcal/m^3 .
- LPG consists of hydrocarbons of such volatility that they can exist as gas under atmospheric pressure but can be readily liquefied under pressure.

Uses:

1. The largest use is as domestic fuel.
2. This is also used widely as an industrial fuel
3. LPG is used as a fuel in certain class of vehicles like trucks and tractors.
4. LPG leaded with tetramethyl lead can be used as the railway diesel locomotives

Disadvantage: Handling has to be done extremely carefully to avoid hazards.

Φ Describe flue gas analysis by Orsat's apparatus method.

Flue gas analysis is carried out by Orsat apparatus method.

Flue gases: A mixture of gases like CO_2 , CO, O_2 & N_2 etc coming out from the combustion chamber is called flue gases.

If the flue gas contains CO, It indicates incomplete combustion.

If the flue gas contains O_2 , It indicates excess supply of air used in combustion.

If the flue gas contains CO_2 , It indicates complete combustion.

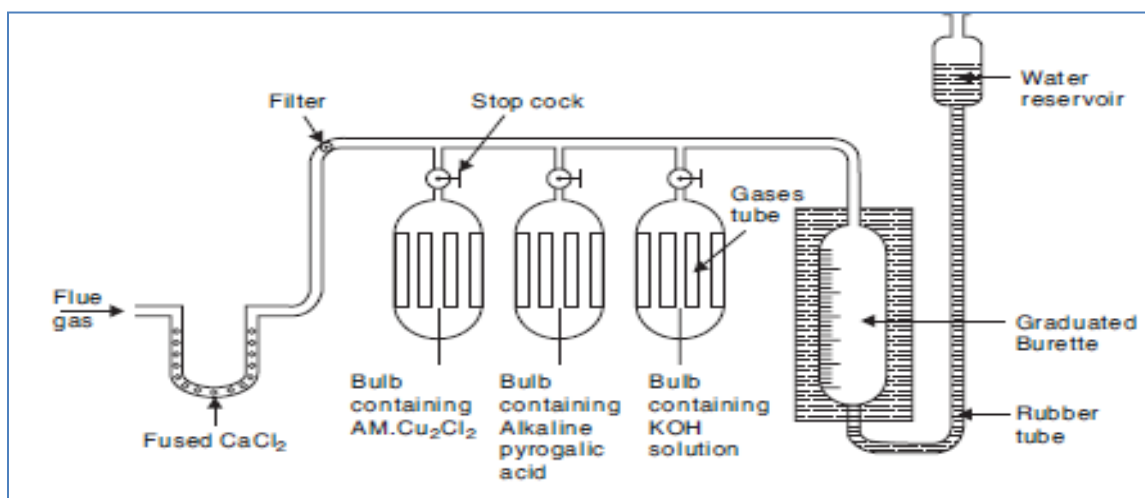
Apparatus: It consists a horizontal tube. At one end of this tube, U tube is connected containing fused CaCl_2 another end is connected through 3 way stop cock. The other end is connected with a graduated burette. The horizontal tube is also connected with 3 different absorption bulbs I, II, III for absorbing CO_2 , CO and O_2 .

I bulb: It contains KOH solutions & it absorbs CO_2 only.

II bulb: It contains Alkaline pyrogallic acid solution & it absorbs CO_2 , & O_2 .

III bulb: It contains Ammoniacal cuprous chloride solution & it absorbs CO_2 , CO & O_2 .

The 3 way stop cock is connected with flue gas supply & it is sucked into the burette & it is adjusted by 100cc. then the 3 way stop cock is closed. In bulb I, CO_2 is absorbed by KOH solution & I is closed & II stopcock is opened, O_2 is absorbed by alkaline pyrogallic acid solution. Now II is closed & III is opened. CO is absorbed by ammonical cuprous chloride. The decrease in volume of the flue gas in the burette indicates the volume of I CO_2 , II O_2 , III CO respectively.



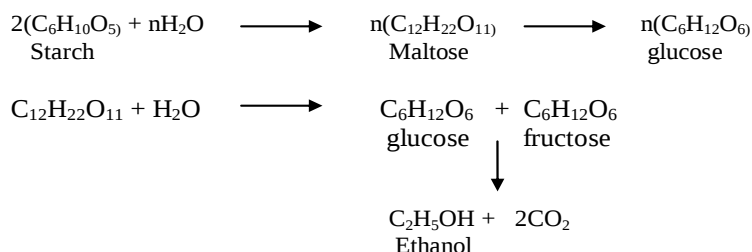
Significance: It gives an clear idea about the complete or incomplete combustion process.

It gives information about efficiency of combustion.

Φ Write a note on Power alcohol?

Definition : When ethyl alcohol is used as fuel in internal combustion engine, it is called as power alcohol.

Preparation:



Advantages of Power Alcohol:

- 1) Ethyl alcohol has good antiknocking property and its octane number is 90, while the octane number of petrol is about 65. Therefore addition of ethyl alcohol to petrol, increases its octane number.
- 2) Alcohol has property of absorbing any traces of water if present in petrol.
- 3) If a specially designed engine with higher compression ratio is used, then the disadvantage of lower C.V. of ethyl alcohol can be overcome.
- 4) Ethyl alcohol contains 'O' atoms, which help for complete combustion of power alcohol and the polluting emissions of CO, hydrocarbon, particulates are reduced largely.
- 5) Use of ethyl alcohol in petrol reduces our dependence on foreign countries for petrol and saves foreign currency considerably.
- 6) Power alcohol is cheaper than petrol.

Disadvantages of Power Alcohol:

- 1) Ethyl alcohol has C.V. 7000 cal/gm much lower than C.V. of petrol 11500 cal/gm. Use of power alcohol reduces power output upto 35%.
- 2) Ethyl alcohol has high surface tension and its atomisation, especially at lower temperatures, is difficult causing starting trouble.
- 3) Ethyl alcohol may undergo oxidation to form acetic acid, which corrodes engine parts.
- 4) Ethyl alcohol obtained by fermentation process directly cannot be mixed with petrol but it has to be dehydrated first.
- 5) As ethyl alcohol contains 'O' atoms, the amount of air required for complete combustion of power alcohol is lesser and therefore carburettor and engine needs to be adjusted or modified, when only ethyl alcohol is used as fuel.

Φ Write a note on Biodiesel?

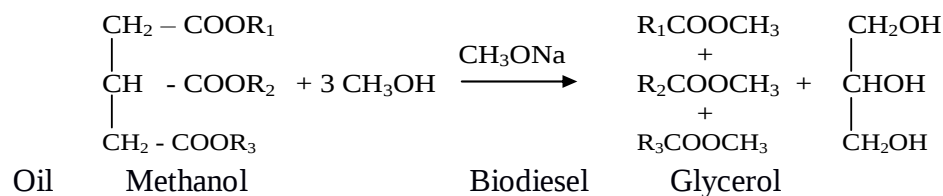
Definition :

Chemically biodiesel is the mixture of methyl esters of long chain carboxylic acids. Biodiesel is obtained by transesterification of vegetable oil or animal fats with methyl alcohol using catalyst sodium metal or sodium methoxide. (Transesterification is the process of converting one ester to another ester).

Reaction for Biodiesel Formation :

During the chemical conversion of vegetable oil to biodiesel we get water soluble glycerol and a small amount of sodium soaps. The water soluble part can be easily separated from biodiesel by washing the mixture with water. The alkaline sodium methoxide catalyst, saponifies some small amount of oil to give soap.

Vegetable Oil + Methanol + Catalyst $\rightleftharpoons$ Biodiesel + Glycerol



Compounds present in biodiesel are like,

methyl palmitate	$\text{H}_3\text{C} - (\text{CH}_2)_{14} - \text{COOCH}_3$
methyl stearate	$\text{H}_3\text{C} - (\text{CH}_2)_{16} - \text{COOCH}_3$
methyl oleate	$\text{H}_3\text{C} - (\text{CH}_2)_7 - \text{CH} = \text{CH} - (\text{CH}_2)_7 - \text{COOCH}_3$
methyl linoleate	$\text{H}_3\text{C} - (\text{CH}_2)_5 - (\text{CH} = \text{CH})_2 - (\text{CH}_2)_7 - \text{COOCH}_3$

Advantages of Biodiesel :

- 1) Biodiesel is cheaper, as it is manufactured from cheap, nonedible or waste oil or animal fats.
- 2) It has high cetane numbers 46 to 54 and high C.V. of about 40 kJ/gm.
- 3) It is regenerative and environment friendly.
- 4) It does not give out particulate and CO pollutants, as 0 atoms in biodiesel help for complete combustion.
- 5) It has certain extent of lubricity, due to higher oiliness of the esters.
- 6) Its use provides good market to vegetable oils and reduces our dependence on diesel on foreign countries, saving currency.
- 7) It is clean to use biodiesel in diesel engines.

Limitations of Biodiesel :

- 1) Cloud and pour points of biodiesel are higher than diesel and can cause problem in fuel flow line. So it cannot be used in cold regions.
- 2) Biodiesel may have dissolving action rubber hoses, gaskets.
- 3) There is shortage of vegetable oils and the starting material if costly, the biodiesel will be costly.
- 4) Biodiesel strongly adheres on metals and can become gummy.

EXPLOSIVES:

- 1) Explosives are the chemical compounds or mixtures, which will on application of an external stimulus such as heat, shock, friction or ignition, undergo rapid chemical decomposition.
- 2) The chemical reaction results in sudden release of large amount of energy due to liberation of gases and temperature.
- 3) The pressure thus released is thrust out equally in all directions.
- 4) Explosives are of immense importance in many peaceful pursuits *e.g.*, in mining, quarrying and pyrotechnics, *etc.*
- 5) Beside these applications, explosives are also used to project lifelines to ships in distress off storm beaten shores or to break roof of burning buildings to save many precious lives
- 6) However, the major use of explosives is in warfare.
- 7) Explosives generally have high nitrogen and oxygen contents which aid the formation of the gaseous products, typically including carbon dioxide, carbon monoxide, oxygen, nitrogen and water vapor.
- 8) All explosive mixtures can be considered to be composed of three components namely fuel, oxidizer and sensitizer.
- 9) Carbon, hydrogen and sulphur, *etc.* provide the essential fuel for the oxygen in the oxidizer.
- 10) Incorporation of a chemical or physical sensitizer enhances the ease with which the explosives can be made to react by means of an initiator.

Classification of Explosives:

Explosives can be classified in many ways according to different criteria.

Based upon velocity :

Based upon type and velocity of explosion involved, explosives have been divided into low and high explosives.

Low explosives:

- 1) A low explosive is a combustible substance that decomposes rapidly (deflagration) and does not explode under normal condition but get detonate through combine use with high explosives.
- 2) Low explosives are normally employed as propellants.

High explosives

- 1) High explosives are detonating explosives.
- 2) The chemical reaction propagates with such rapidity that the rate of reaction zone into the material exceeds velocity of sound.
- 3) High explosives are normally employed in mining, demolition and military warheads. They undergo detonation at rates of 1,000 to 9,000 m/s.

Based upon sensitivity:

Based upon sensitivity of the chemical explosives to the external environment like heat, shock and friction, these can be categorized as follows

Primary explosives:

- 1) They are extremely sensitive to shock, friction and heat.
- 2) They will burn rapidly or detonated, if ignited.
- 3) Primary (or initiating) explosives are used to start the explosion.
- 4) Primary explosives explode or detonate when they are heated or subjected to shock.
- 5) Examples include mercury fulminate, lead azide, lead salts of picric acid and trinitroresorcinol.
- 6) Primary explosives are often used to detonate a secondary explosive because their detonation is rapid and powerful enough to produce a shock wave that can detonate another explosive.

Secondary explosives:

- 1) These are also called base explosives and are relatively insensitive to shock, friction and heat.
- 2) Secondary explosives are the main charge. They burn when ignited in small unconfined quantities but detonation can occur.

Numerical problems:

- 1) A sample of the Gondwana Coal of Jharia was analysed as follows: Exactly 2.500g was weighed into a silica crucible. After heating for 1 hour at 110°C , the residue weighed 2.415g. The crucible was then covered with a vented lid and strongly heated for exactly 7 minutes at $950 \pm 20^{\circ}\text{C}$. The residue weighed 1.528g. The crucible was then heated without the cover, until a constant weight was obtained. The last residue was found to weigh 0.245 g. (i) Calculate the percentage result of the above analysis (ii) To which type of analysis does the above description belong? Why is the analysis so-named?
Ans: (Moisture = 3.4%; volatile matter = 35.48%; ash = 9.80%; and fixed C = 51.32%).
- 2) 1.0 g of a sample of coal was used for nitrogen estimation by Kjeldahl method. The evolved ammonia was collected in 25 mL (N/10) sulphuric acid. To neutralize excess acid, 10 mL of 0.1 N sodium Hydroxide was required. Determine the percentage of nitrogen in the given sample of coal.
- 3) 0.5g of a sample of coal was used in a bomb calorimeter for the determination of calorific value. Calorific value of coal was found to be 6800 cal/g. The ash formed in the bomb calorimeter was extracted with acid and the acid extract was heated with barium nitrate solution and a precipitate of barium sulphate was obtained. The precipitate was filtered, dried and weighed. The weight of precipitate was found to be 0.05 g. Calculate the percentage of sulphur in the coal sample. **Ans:** (1.3734%).
- 4) A sample of coal was analysed as follows: 1.000g of an air-dried coal sample was weighed in a silica crucible. After heating for 1 hour at $105-110^{\circ}\text{C}$, the dry coal residue weighed 0.985 g. The crucible was covered with a vented lid and then heated strongly for exactly 7 minutes at $950 \pm 20^{\circ}\text{C}$. The residue weighed 0.800g. The crucible was then heated strongly in air, until a constant weight was obtained. The last residue was found to weigh 0.100g. Calculate the proximate analysis. **Ans:** (Moisture = 1.5; volatile matter = 18.5; ash = 10.0; and fixed C = 70.0%).
- 5) Calculate the gross calorific value and net calorific value of coal sample having the following composition: C = 80%, H = 7%, O = 3%, S = 3.5%, N = 2.1% and ash = 4.4% **Ans:** (8828, 8458 cal/g).
- 6) Calculate the higher and lower calorific value of a coal sample containing 84% of carbon, 1.5% of sulphur, 0.6% of nitrogen, 5.5% of hydrogen and 8.4% of oxygen. **Ans:** 8,356 kcal/kg, 8,066 kcal/kg.
- 7) Calculate the gross and net calorific value of coal having the following compositions: carbon = 85%, hydrogen = 8%, sulphur = 1%, nitrogen = 2%, ash = 4%, latent heat of steam is 587 cal/g.
Solution: [Hint According to Dulong's formula, Gross Calorific Value (GCV) or Higher Calorific Value (HCV) is $\text{The percentage of O is } 100 - [\text{percentage of C} + \text{H} + \text{S} + \text{N} + \text{Ash}]$. From the above data, Percentage of O is 0]
ANS. H.C.V. = 9,650.4 kcal/kg; Net Calorific Value (NCV) = 9,227.8 kcal/kg.
- 8) Calculate the gross and net calorific value of coal having the following composition: Carbon: 85% Hydrogen: 8% Sulphur: 1% Nitrogen: 2% Oxygen: 2% Ash: 2% and Latent heat of steam: 587 cal/g.

- 9) Calculate the higher (gross) and lower (net) calorific values of a coal sample containing 84% carbon; 8% hydrogen; 1.5% sulphur; 2% nitrogen and remaining is ash.
- 10) Calculate the higher (gross) and lower (net) calorific values of a coal sample containing 67% carbon; 7% hydrogen; 4% oxygen; 3.5% sulphur; 2% nitrogen and remaining is ash.
- 11) Calculate the higher (gross) and lower (net) calorific values of a coal sample containing 78% carbon; 4% hydrogen; 5% oxygen; 2.5% sulphur; 2% nitrogen and remaining is ash.
- 12) 0.25 gm of a coal sample on burning in a combustion chamber in the current of pure oxygen was found to increase weight of U-tube with anhydrous CaCl_2 by 0.075 gm and of KOH U-tube by 0.52gm. Find C and H percentages in coal.
- 13) One gram of coal sample was burnt in oxygen. Carbon Dioxide was absorbed in KOH and water vapour in CaCl_2 . The increase in weight of KOH and CaCl_2 was 3.157 and 0.504 gm respectively. Determine % C and % H in the sample.
Ans: (C % = 86.1, H% = 5.6)
- 14) Find the % of C and H in coal sample from the following data- 0.20 gm of coal on burning in a combustion tube in presence of pure oxygen was found to increase in the weight of CaCl_2 tube by 0.08 gm and KOH tube by 0.12 gm.